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PHASE TRANSFORMATIONS AND CORROSION OF ZIRCONIUM-COPPER-MOLYBDENUM ALLOYS

by

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ABSTRACT

The transformation reactions for a Zr-1%Cu-1.5% Mo alloy quenched from the beta phase (1000°C) and aged at 500°C were shown to be:

$$\text{omega} + \text{beta} \rightarrow \text{alpha prime} \rightarrow \text{equilibrium alpha} + Zr_2Cu + ZrMo_2$$

The corrosion resistance of this alloy, and of a Zr-0.5%Cu-0.5%Mo alloy, were found to be related to the microstructures resulting from the transformation reaction. Optimum corrosion resistance was obtained after ageing for 33 and 24 hr respectively.

Ageing resulted in an increase in the size of the intermetallic particles, and larger $ZrMo_2$ particles in overaged specimens corroded at a rate greater than the matrix, causing cracking of the corrosion film and resulting in an accelerated corrosion rate for the specimens.

The type of corrosion film, like the corrosion rate, was affected by changes in the microstructure that occurred during transformation.

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1. INTRODUCTION

The low thermal neutron-capture cross section of zirconium, coupled with good mechanical properties and corrosion resistance, have made this metal of practical interest in nuclear engineering. The work presented in this paper was part of a study of zirconium-copper-molybdenum alloys. The purpose of the investigation was to study the transformation reactions occurring during ageing of solution heat-treated alloys and to determine the effect of heat treatment on their corrosion behaviour in steam.

2. EXPERIMENTAL PROCEDURE

2.1 Alloy Preparation

Alloys of the following compositions were prepared in the laboratory for investigation:

Zr-0.5%Cu - 0.5% Mo, Zr-1% Cu - 1.5% Mo and Zr-3% Cu - 4.5% Mo

The alloys were made with reactor-grade zirconium sponge, OFHC copper and 99.5% pure molybdenum. Melting and alloying were carried out in a tungsten-arc furnace in an argon atmosphere. Each alloy was remelted at least four times to ensure homogeneity. The final ingot was cigar-shaped and weighed approximately 75 grams.

The laboratory-prepared alloys, except Zr-3% Cu - 4.5% Mo, were hot-swaged in air at 700°C to 0.35-in.-diameter rods. Some rods were hot-rolled at 700°C to sheet 0.20 in. thick.

The Zr-3% Cu - 4.5% Mo composition was prepared to facilitate identification of intermetallic phases.

In addition to the laboratory-prepared material, tests were also carried out on Zr-1% Cu - 1.5% Mo alloy sheet (0.062 in. thick) of commercial origin.

2.2 Study of Transformation Reactions

Specimens for transformation-reaction studies were taken from the hot-rolled Zr-1% Cu - 1.5% Mo alloy and heat treated in vacuum for 1 hr at temperatures ranging from 800°C to 1000°C, followed by water quenching. The specimens quenched from 1000°C were aged at 500°C for 2, 8 and 30 min and 1, 4, 48 and 100 hr. Microexamination and X-ray diffraction analysis were carried out on all specimens.

2.3 Identification of Intermetallic Phases

Specimens of the Zr-1% Cu - 1.5% Mo material were examined by an electron-probe microanalyzer to determine the composition of the intermetallic phases. Some specimens were solution heat treated in vacuum for 1 hr at 1000°C, water quenched, then aged at 500°C for 100 hr; in an attempt to coalesce the intermetallics, a specimen was heat treated in vacuum at 1000°C for 1 hr, then cooled at 5.5°C/hr to 550°C and water quenched. A specimen of the Zr-3% Cu - 4.5% Mo alloy in the arc-melted condition was also examined.

2.4 Corrosion Testing

Corrosion tests were carried out in an autoclave in steam at 400°C and 1500 psi for times up to 400 hr. Specimens were removed periodically for weighing, at which time the water was changed.

2.5 Examination of Corrosion Films

Microexamination was made of cross sections of corrosion films on Zr-1% Cu - 1.5% Mo alloy specimens that were tested for 400 hr in the following heat-treated conditions:

(a) 1 hr in vacuum at 1000°C and water quenched;

(b) 1 hr in vacuum at 1000°C, water quenched, and then aged at 500°C for times up to 100 hr.

Formvar replicas, for electron microscopy, were made of the corrosion films on specimens of the Zr-0.5% Cu - 0.5% Mo swaged bars that had been corrosion tested for 24 hr in the following heat-treated conditions:

(a) 1 hr in vacuum at 1000°C and water quenched;

(b) 1 hr in vacuum at 1000°C, water quenched, and then aged at 500°C for 24 hr and 100 hr;

(c) 1 hr anneal in vacuum at 700°C

The structures of these specimens, before corrosion testing, were also examined by electron microscope.

2.6 Polishing and Etching

For microexamination, X-ray diffraction analysis and electron-probe microanalysis, specimens were polished on silicon carbide abrasive paper to a 600 grit and then on microcloth with Linde A compound as the abrasive. This was followed by chemical polishing in a solution containing 45 cc nitric acid, 45 cc distilled water and 8-10 cc hydrofluoric acid.

To etch for the Zr-Mo intermetallic, which was also visible after chemical polishing, specimens were immersed for 30 sec in a solution containing 20 cc hydrofluoric acid, 20 cc nitric acid and 60 cc glycerine. To reveal only the Zr-Cu intermetallic, polished specimens were immersed for 30 sec in a solution containing 1 cc hydrofluoric acid, 1 cc nitric acid and 98 cc distilled water.

3. EXPERIMENTAL RESULTS

3.1 Transformation Reactions

X-ray diffraction analysis of Zr-1%Cu - 1.5%Mo specimens quenched from 800°C showed the structure to consist of alpha, omega (a transformation phase) and beta phases. Metallographic examination of these specimens revealed pools of equilibrium alpha that had been retained from the quenching temperature. This structure is illustrated in Figure 1.

Specimens heat treated at 850°C and 900°C had similar structures to those heat treated at 800°C, except that the amount of alpha phase present

decreased as the heat-treating temperature increased.

When specimens were quenched from 1000°C, there was no alpha visible in the microstructure, and X-ray diffraction analysis showed this quenched structure to consist mainly of the omega phase with a small amount of beta phase.

Results of X-ray diffraction analysis and microexamination of specimens water quenched from 1000°C and aged at 500°C for different times are listed in Table 1. Omega and beta phases were present after quenching but transformed to alpha-prime on ageing for 8 min. After ageing for 30 min intermetallics began to precipitate, and after 4 hr the alpha-prime had transformed to equilibrium alpha. An increase in the amount of intermetallics with ageing time can be seen by comparing the photomicrographs in Figures 2 and 3, showing specimens of the Zr-1%Cu-1.5%Mo alloy aged for 4 and 48 hr, respectively.

3.2 Intermetallic Phases

Intermetallics present in Zr-1%Cu-1.5% Mo alloy specimens heat treated at 1000°C for 1 hr and aged at 500°C for 100 hr were identified by electron probe as Zr-Mo and Zr-Cu phases, but the particles were not large enough for quantitative analysis. The two phases were revealed by selective etching, as shown by Figures 4 and 5.

Electron-probe microanalysis of the specimen heat treated at 1000°C for 1 hr, cooled at 5.5°C/hr to 550°C and then water quenched, showed one

intermetallic phase to be Zr_2Cu, but the Zr-Mo phase could not be identified. This heat treatment, which was intended to coalesce the intermetallics, caused the Zr_2Cu phase to precipitate as particles and the Zr-Mo phase to be distributed along alpha-platelet boundaries.

Electron-probe microanalysis of an arc-melted specimen of the Zr-3% Cu - 4.5% Mo alloy identified a $ZrMo_2$ phase. The $ZrMo_2$ in this specimen was present as particles (Figure 6) surrounded by the Zr_2-Cu (Figure 7). Electron-probe scanning X-ray images of this alloy confirmed the presence of the molybdenum-, copper-, and zirconium-rich phases.

3.3 Corrosion Testing

Results of the corrosion tests on the Zr-1% Cu - 1.5% Mo and Zr-0.5% Cu - 0.5% Mo alloys are shown in Figure 8 as plots of weight gain versus time of ageing at 500°C. The weight gain for both alloys varied considerably with ageing time. The curves were parabolic, with a minimum corrosion rate occurring at 24 hr for Zr-0.5%Cu - 0.5% Mo and at 33 hr for Zr-1% Cu - 1.5% Mo.

Short corrosion times (300-400 hr) were used to determine the curves because the corrosion film on some of the specimens - particularly those aged for longer periods - began to spall if the tests were continued for longer times.

3.4 Corrosion Films: Zr-1% Cu - 1.5% Mo Alloy

Corrosion films on specimens of the Zr-1% Cu - 1.5% Mo alloy, after testing for 400 hr, were of four distinct types, depending on the ageing time.

1. Films on specimens in the as-quenched condition, and on specimens aged less than 8 min, had a mottled appearance. A cross section of this film (Figure 9) shows a difference in film thickness on adjacent grains, and anodizing of this specimen revealed that the grains had different orientations.

2. Specimens aged for 30 min to 4 hr had a black film. Figure 10 illustrates a cross section of this film.

3. Specimens aged for 24 and 48 hr had a thin, black film, with a white, adherent film forming at some locations over the black. A cross section of this black film is shown in Figure 11.

4. After ageing for 72 hr and 100 hr, corrosion specimens acquired a white film that had a tendency to spall. Figure 12 shows a cross section of the white film.

Information on these four corrosion films is given in Table 2.

3.5 Microstructure and Corrosion Films: Zr-0.5% Cu - 0.5% Mo Alloy

Figures 13 to 16 are electron micrographs of the Zr-0.5% Cu -0.5% Mo alloy in various heat-treated conditions.

Figure 13 shows that there were few intermetallic particles in specimens quenched from 1000°C. On ageing, intermetallic particles began to appear; their size increased with time and their number also increased initially, then decreased (Figures 14-15). The largest intermetallic particles were present in the annealed specimens, the microstructure of which is shown in Figure 16. Preferential etching indicated that these particles were $ZrMo_2$.

After being corrosion tested for 24 hr, the zirconium oxide film remained adherent on specimens quenched from 1000°C and on specimens aged for 24 hr (Figures 17 and 18, respectively). However, in the case of the specimens containing large particles, i.e., those aged for 100 hr (Figure 15) and those annealed at 700°C (Figure 16), the corrosion film broke up because of cracking around enlarged intermetallic particles (Figures 19-20).

4. DISCUSSION

4.1 Transformation Reactions

Specimens of the Zr-1% Cu - 1.5% Mo alloy quenched from 800°C, 850°C and 900°C contained alpha, beta and omega phases, indicating that they had been in the alpha + beta phase region. Specimens quenched from 1000°C contained only the omega and beta phases indicating they had been in the beta phase region. The copper and molybdenum were held in solid solution in all these specimens.

It has been shown that on ageing for 8 min, the omega and beta phases transformed to alpha prime, which also retained the copper and molybdenum in solid solution (Table 1). On further ageing, intermetallics began to appear and the X-ray diffraction lines of the alpha-prime phase gradually transformed to the sharp lines of equilibrium alpha phase.

It is concluded that the transformation reactions of the Zr-1% Cu-1.5% Mo alloy, after quenching from 1000°C and ageing at 500°C, are as follows:

omega + beta → alpha prime → equilibrium alpha + intermetallics

4.2 Intermetallic Phases

From the phase rule, the maximum number of intermetallic phases that can be present in the Zr-Cu-Mo alloys examined is two. Results from electron-probe microanalysis of heat-treated specimens of the Zr-1% Cu - 1.5% Mo alloy showed the presence of two intermetallics, namely, Zr_2Cu and a Zr-Mo phase that could not be identified because of its unfavourable distribution. In Zr-3% Cu-4.5% Mo specimens, the Zr-Mo phase appeared as particles large enough for identification as $ZrMo_2$ (Figure 6).

As there is only one intermetallic phase in the Zr-Mo system, i.e., $ZrMo_2$, and because this phase was identified in Zr-3% Cu-4.5% Mo arc-melted specimens, it would appear that $ZrMo_2$ is the intermetallic phase present in Zr-1% Cu - 1.5% Mo alloy specimens.

4.3 Corrosion

When Zr-1% Cu - 1.5% Mo specimens were water quenched from 1000°C, the copper and molybdenum were held in solid solution in the omega and beta phases (Table 1) and, as shown by the electron micrograph in Figure 13, the copper and molybdenum were also held in solid solution in the Zr-0.5% Cu - 0.5% Mo alloy specimens quenched from 1000°C. It can be concluded from corrosion rates of the quenched specimens of both these alloys (Figure 8) that the presence of copper and molybdenum in solid solution is unfavourable for good corrosion resistance.

As ageing commenced and fine intermetallics began to appear, the corrosion resistance improved. The improved corrosion resistance at this stage is obviously related to the change in structure from the omega plus beta to alpha and to the presence of fine intermetallics. On further ageing, as the $ZrMo_2$ particles increased in size, they corroded at a faster rate than the matrix and, eventually, because of their size, caused cracking in the corrosion film. This resulted in an increase in the corrosion rate of the specimen.

There was no evidence that Zr_2Cu had any influence on the corrosion behaviour of the alloys.

4.4 Types of Corrosion Film

The mottled appearance of the corrosion film on Zr-1% Cu-1.5% Mo specimens aged for less than 8 min was a result of the variation in corrosion

rate on grains with different orientations. Because the specimens were predominantly omega, this would indicate that the omega phase had anisotropic corrosion properties.

As ageing progressed, the corrosion resistance increased, and the thickness of the film decreased. After ageing for 48 hr, the black film was only 3 microns thick (Table 2).

The white film on specimens aged for longer periods (72 and 100 hr) most likely resulted from accelerated corrosion of the $ZrMo_2$ particles, causing cracking of the corrosion film and, therefore, increased corrosion rates.

The type of corrosion film, then, like the corrosion rate, was dependent on the heat treatment. This is emphasized by comparing the dark film on specimens of the Zr-1% Cu - 1.5% Mo alloy aged for 48 hr (Figure 11) with the white film, on specimens aged for 100 hr (Figure 12).

5. CONCLUSIONS

1. The presence of two intermetallic compounds in the Zr-Cu-Mo alloys was established. One intermetallic was positively identified as Zr_2Cu and the other was tentatively identified as $ZrMo_2$.

2. The zirconium alloy Zr-1% Cu - 1.5% Mo aged according to the reactions:

omega + beta → alpha prime → equilibrium alpha

+ Zr_2Cu + $ZrMo_2$

when water quenched from the beta phase (1000°C) and aged at 500°C.

3. The weight gain of specimens of the Zr-1%Cu - 1.5%Mo alloy during corrosion testing at 400°C and 1500 psi varied considerably with heat treatment. Minimum weight gains were observed after specimens were aged for 33 hr.

4. The corrosion rate of the Zr-0.5%Cu - 0.5%Mo alloy was also shown to depend on the heat treatment. The minimum corrosion rate for this alloy was obtained with specimens aged for 24 hr.

5. The omega phase in the quenched structure of the Zr -1%Cu - 1.5%Mo alloy specimens had anisotropic corrosion properties.

6. Depending on the heat treatment given the Zr-1%Cu - 1.5%Mo alloy, four different types of corrosion film were observed.

7. Overageing of the Zr-0.5%Cu - 0.5%Mo alloy resulted in an increase in the size of the $ZrMo_2$ particles. These particles corroded faster than the matrix and eventually, because of their size, caused cracking in the corrosion film, resulting in an accelerated corrosion rate for the specimens.

ACKNOWLEDGEMENTS

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CFD/HMS/gm

TABLE 1

Phases Present in Zr-1.0% Cu - 1.5% Mo Alloy
(Quenched from 1000°C, Aged at 500°C)

Ageing Time	Phases Present
0	Omega + small amount of beta
2 min	Omega + small amount of beta
8 min	Alpha prime
30 min	Alpha prime + intermetallics
1 hr	Alpha prime + intermetallics
4 hr	Alpha + intermetallics
48 hr	Alpha + intermetallics
100 hr	Alpha + intermetallics

TABLE 2

Corrosion Films on Zr-1.0% Cu - 1.5% Mo Alloy
After 400 hr in Steam at 400°C and 1500 psi

Ageing Time	Film Appearance	Film Thickness (microns)	Wt Gain of Specimens (mg/dm^2)*
0.	Mottled	42 and 56	725
4 hr	Black	42	400
48 hr	Black & white	3 (black)	80
100 hr	White	96	1150

* Average of two specimens.

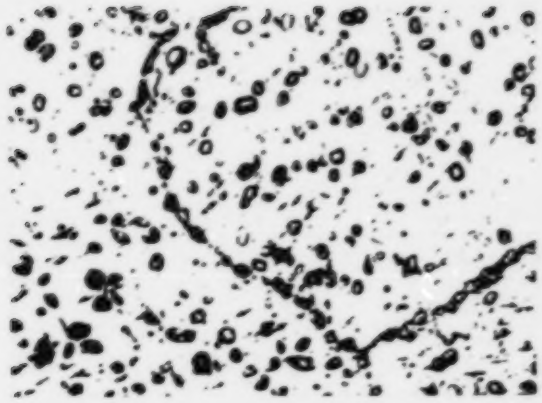

Figure 1. Zr - 1% Cu - 1.5% Mo.
Heat treated 800°C, water quenched.
As-polished (X750).

Figure 2. Zr - 1% Cu - 1.5% Mo.
Quenched from 1000°C, aged
500°C for 4 hr.
As-polished (X750).

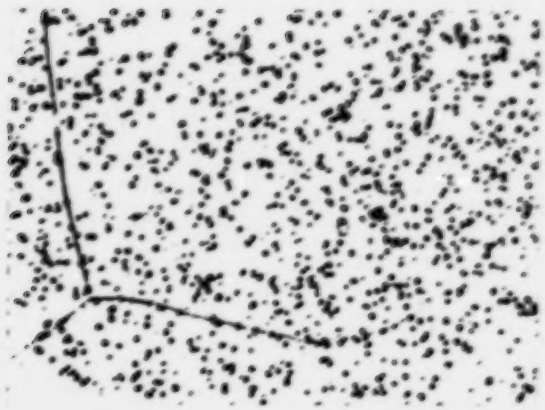

Figure 3. Zr - 1% Cu - 1.5% Mo.
Quenched from 1000°C, aged
500°C for 48 hr.
As-polished (X750).

Figure 4. Zr - 1% Cu - 1.5% Mo.
Heat treated 1000°C for 1 hr, water
quenched, aged 500°C for 100 hr.
Etched for Zr-Mo phase (X1000).

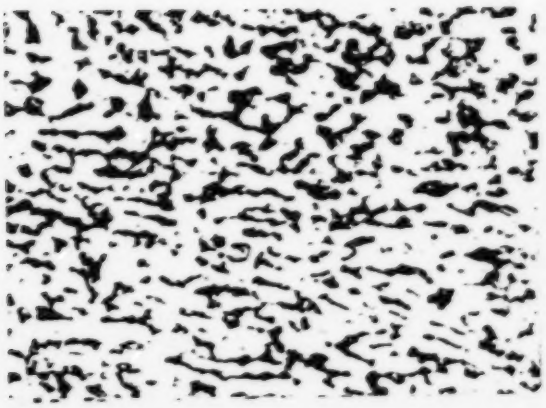

Figure 5. Zr - 1% Cu - 1.5% Mo.
Heat treated 1000°C for 1 hr, water quenched, aged 500°C for 100 hr.
Etched for Zr-Cu phase (X1000).

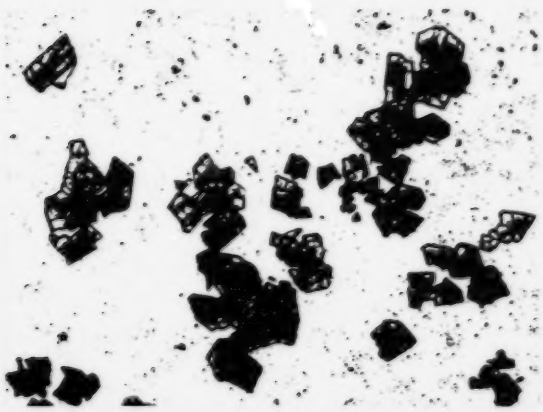

Figure 6. Zr-3% Cu - 4.5% Mo.
Arc melted.
Etched for Zr-Mo phase (X400).

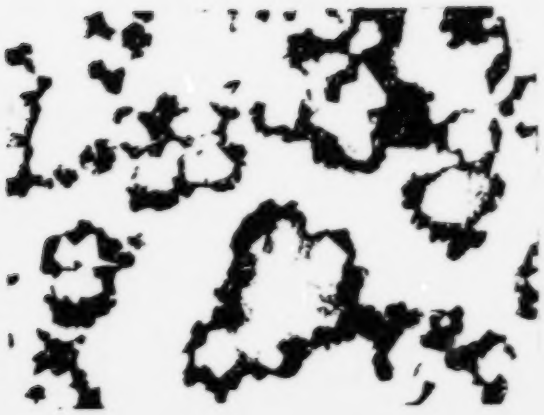

Figure 7. Zr - 3% Cu - 4.5% Mo.
Arc melted.
Etched for Zr-Cu phase (X400).

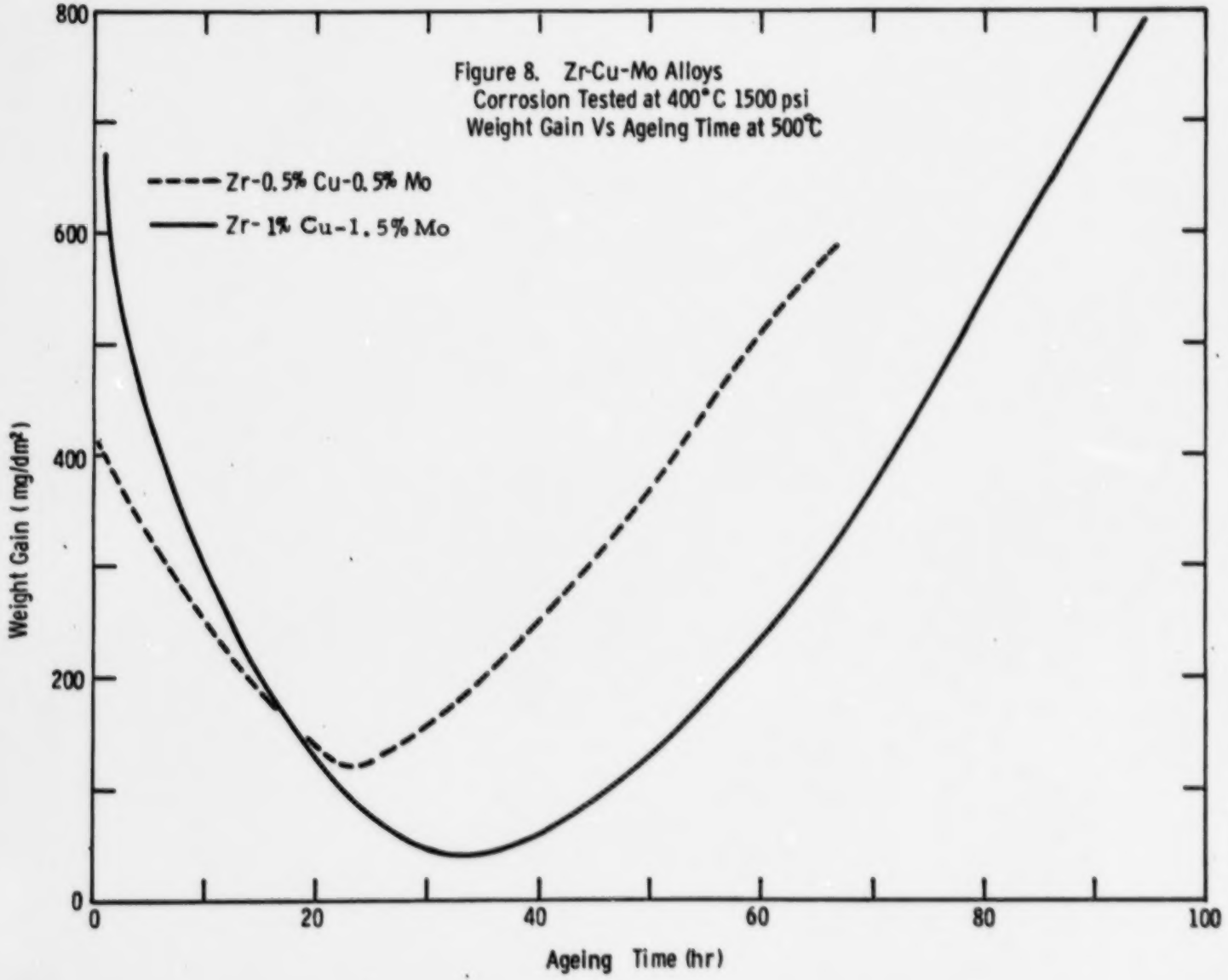
Figure 8. Zr-Cu-Mo Alloys
Corrosion Tested at 400°C 1500 psi
Weight Gain Vs Ageing Time at 500°C
Zr-0.5% Cu-0.5% Mo
Zr-1% Cu-1.5% Mo
Weight Gain (mg/dm²)
Ageing Time (hr)
0
200
400
600
800
0
20
40
60
80
100

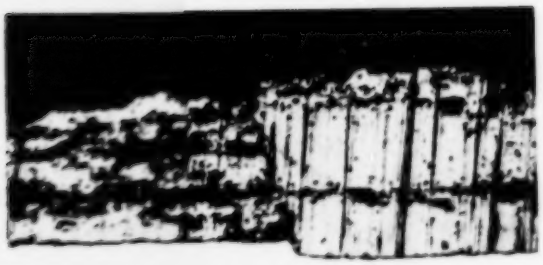

Figure 9. Zr - 1% Cu - 1.5% Mo.
Quenched from 1000°C, corrosion tested 400°C and 1500 psi for 400 hr.
Cross section, mottled film.
As-polished (X500).

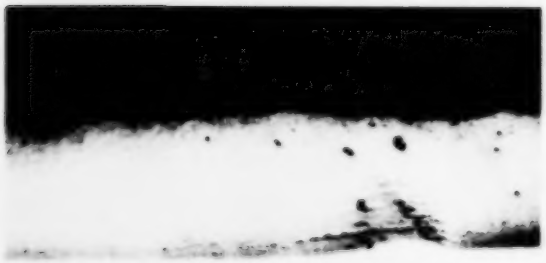

Figure 10. Zr - 1% Cu - 1.5% Mo.
Quenched from 1000°C, aged 500°C for 4 hr; corrosion tested 400°C and 1500 psi for 400 hr. Cross section, black film. As-polished (X500).

Figure 11. Zr - 1% Cu - 1.5% Mo.
Quenched from 1000°C, aged 500°C for 48 hr;
corrosion tested 400°C and 1500 psi for 400 hr.
Cross section, black film.
As-polished (X500).

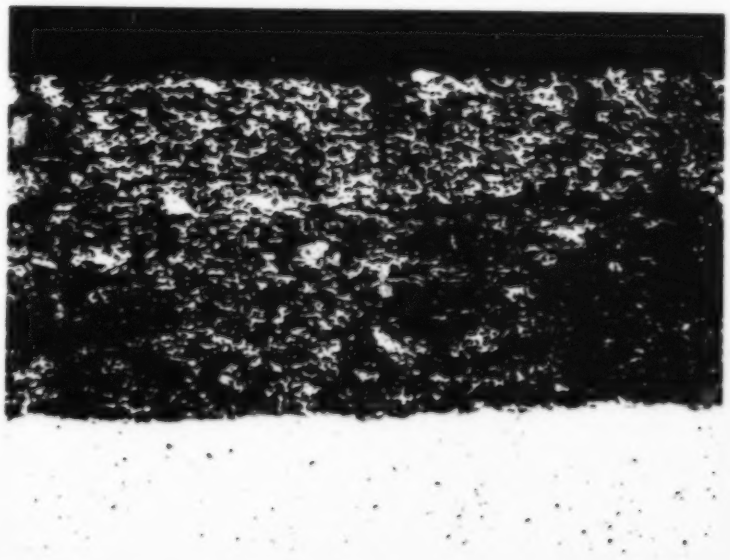

Figure 12. Zr - 1% Cu - 1.5% Mo.
Quenched from 1000°C, aged 500°C for 100 hr;
corrosion tested 400°C and 1500 psi for 400 hr.
Cross section, white film.
As-polished (X500).

Figure 13. Zr - 0.5% Cu - 0.5% Mo.
Quenched from 1000°C.
As-polished (X10, 000).

Figure 14. Zr - 0.5% Cu - 0.5% Mo.
Quenched from 1000°C, aged 500°C for 24 hr.
As-polished (X10, 000).

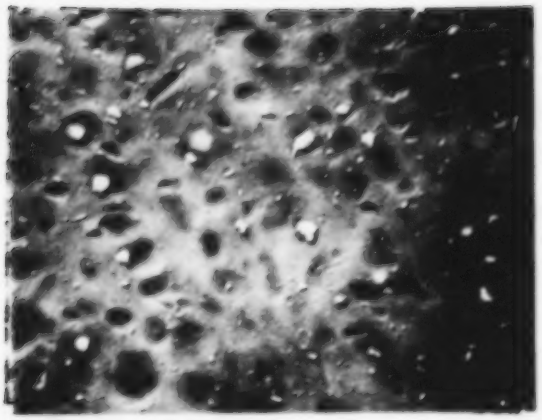

Figure 15. Zr - 0.5% Cu - 0.5% Mo.
Quenched from 1000°C, aged 500°C for 100 hr.
As-polished (X 10,000).

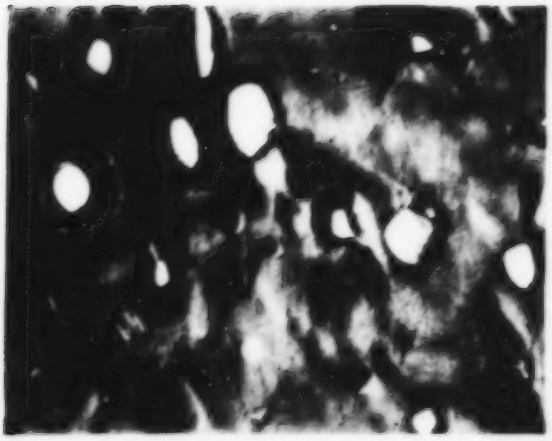

Figure 16. Zr - 0.5% Cu - 0.5% Mo.
Annealed 700°C for 1 hr.
As-polished (X 10,000).

Figure 17. Zr - 0.5% Cu - 0.5% Mo alloy, corrosion film. Quenched 1000°C; corrosion tested 24 hr. (X 10,000).

Figure 18. Zr - 0.5% Cu - 0.5% Mo alloy, corrosion film. Quenched from 1000°C, aged 500°C for 24 hr; corrosion tested 24 hr. (X 10,000).

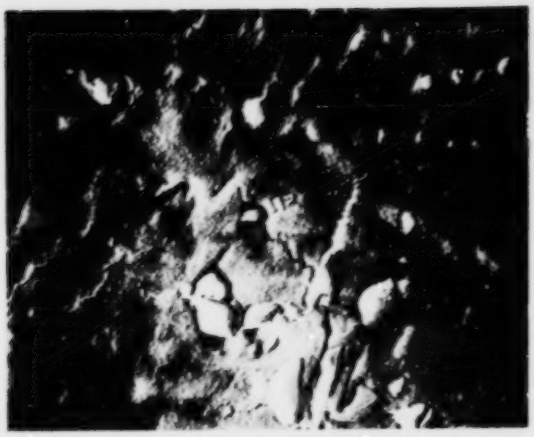

Figure 19. Zr - 0.5% Cu - 0.5% Mo alloy, corrosion film. Quenched from 1000°C, aged 500°C for 100 hr; corrosion tested 24 hr. (X 10,000).

Figure 20. Zr - 0.5% Cu - 0.5% Mo alloy, corrosion film. Annealed 700°C for 1 hr; corrorion tested 24 hr. (X 10,000).